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I. ADSORPTION

One of the earliest applications of radioactive isotopes was in the study of adsorption. The principal lines of investigation based on this method were: (1) investigation of adsorption laws, particularly those of adsorption equilibrium, at minimal coverage of the surface, (2) study of the adsorption of mixtures, (3) study of surface inhomogeneity by means of differential isotope adsorption, and (4) investigation of the properties of substances adsorbed on active catalysts.

Aside from these four theoretical subdivisions, a problem of great practical interest which has been thoroughly investigated is the capture by freshly formed precipitates or crystalline sorbents of small quantities of substances from solution. Only the use of radioactive tracers has permitted some clarification of this complex phenomenon, so that it could be separated into simple component processes. The work of Soviet radiochemists headed by V. G. Khlopin is particularly outstanding in this field.

Investigations conducted by members of this group demonstrated first that, to be co-precipitated, components which are present in small quantities must be isomorphous with the carrier precipitate. Khlopin, Polesitskiy, Ratner, Tolmachov, et al. (8, 9), showed that the distribution of the microcomponent between crystals and the solution follows the Berthelot-Nernst law when equilibrium has been reached and conforms to the logarithmic Doerner-Hoskins law [cf. J. Am. Chem. S. 47, 662, 1925] in the case of nonequilibrium systems. Khlopin proved experimentally that in the capture of small quantities of substances by solids the adjustment of the concentration of microcomponents in crystals proceeds over recrystallization of the latter in solution (10). This refuted Tamman's theory that diffusion plays an exclusive role in this process.

Khlopin and Nikitin clarified the nature of Grimm's type of isomorphism and of its differences from the classical type (11). It was shown that the absence of mixed crystal formation below a certain concentration of the microcomponent is typical of Grimm's isomorphism. The microcomponent presumably replaces whole regions of the crystal lattice under these conditions. The theory of distribution of microcomponents between the solid and the liquid phase was developed by Ratner (12).

The method of measuring surfaces of crystal suspensions with the aid of radioactive indicators is dealt with below. It is closely connected with the isolation of microcomponents. The important problem involved here, which has been briefly indicated, is of interest from another point of view and will not be considered in this paper.

A. Use of Radioactive Tracers in Determination of the Absolute Surface of Crystal Suspensions

There are three methods for measuring a surface with the aid of radioactive indicators. The first is based on the exchange of an inactive ion entering into the composition of the solid phase with its radioactive isotope contained in a saturated solution. The second involves the exchange of an inactive ion entering the composition of the solid phase with its radioactive isotope contained in the isomorphously crystallized part of the solid phase. The third method is based on measurement of the emanation of a radioactive substance which is distributed homogeneously throughout the solid phase. The first two methods originated with Paneth, while the third was proposed by Hahn (compare review listed under Item 13 in bibliography).

The results obtained by the first two methods frequently deviate in both directions from the true result. If only a fraction of the surface participates

- 2 -

SECRET

SECRET

50X1-HUM

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SECRET

in the exchange, a value which is too low will be obtained. If layers lying below the surface participate, the value will be too high. Khlopin and Merkulova (14) studied the limitations of the three methods and clarified the conditions under which they can be applied. The investigation in question was carried out with suspensions of the following crystals: lead sulfate, barium sulfate, lead chromate, barium chromate, and silver chromate. As the radioactive isotope of lead, RaD was used; radium was used as an ion supposedly isomorphous with ions of lead and barium; and RaD was used as an ion supposedly isomorphous with silver. In the case of suspensions of PbSO_4 , BaSO_4 , and BaCrO_4 , there is good agreement between the results obtained by the three methods in question. In the case of silver chromate, the method of exchange with RaD ions leads to a value which is much too high. The authors doubt for that reason that PbCrO_4 and Ag_2CrO_4 are actually isomorphous. They reached the conclusion that radioactive tracer methods are of value when the surface is clean and there are no extraneous adsorbed ions. The exchange with the surface atomic layer is completed rapidly (within the first 15 minutes), whereupon a secondary exchange with inner layers, which is accompanied by recrystallization, takes place. For the application of the method of exchange with an "isomorphous" ion, a knowledge of the crystallization coefficient of the system at the temperature in question is needed. This coefficient enters into the appropriate formula instead of Paneth's solubility ratio.

Khlopin and Merkulova developed a special relationship according to which the ratio of the quantity of inactive ion on the surface to the quantity of that ion in the saturated solution is proportional to the ratio of the quantity of the adsorbed radioactive "isomorphous" ion to the quantity of the latter ion in the solution. The coefficient of proportionality is equal to the crystallization coefficient of the system in question.

In the emanation method, one must be sure that the radioactive material evolving the emanation is distributed completely and uniformly. The correction for the diffusion of the emanation through the crystal lattice, as applied by Strassman, is unnecessary. Khlopin and Kuznetsova (15) call attention to the fact that, in the adsorption of radium on lead sulfate, foreign ions in solution may bring about rapid recrystallization. There is also additional deposition of solid material due to the altered solubility caused by changed concentration of the corresponding ions in solution. Both factors are a source of error. The slow process of the capture of radium ions which follows the rapid process of adsorption is connected with the slow process of combined crystallization taking place in consequence of the recrystallization of the solid phase. L. Ymre (Z. phys. Chem., 1931, A. 153, 127, 138) was mistaken in assuming that the slow process is essentially a slow stage of the adsorption process itself.

Radioactive tracer methods can also be applied in the measurement of metal surfaces (O. Hahn, Applied Radiochemistry, Goskhimizdat, 1947). The relationships expressed by Merkulova and Khlopin retain their full validity here.

Early work in the field was concerned principally with the exchange adsorption of "isomorphous" ions or the potential-forming adsorption of the ordinary ion already present, because the isolation of substances present in low concentrations is based on processes of this type. A considerable number of papers dealing with the adsorption of radon from the gas phase have been published. The qualitative relationships established in that type of work are covered in Section B, below.

B. Investigation of Adsorption Laws

At low degrees of filling of the surface the adsorption isotherm follows Henry's law. A higher degree of filling results in Langmuir's isotherm. Inhomogeneities of surface properties and of surface forces in the adsorption layer must lead to still other types of isotherms. Even at low degrees of filling or coverage of the surface, conditions corresponding to Henry's law

- 3 -

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SECRET

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SECRET

50X1-HUM

cannot always be reached. Often the parabolic isotherm

$$q = A p^{1/n}$$

or the logarithmic isotherm of Shlygin and Frumkin (16)

$$q = B \lg p$$

most accurately describes the adsorption equilibrium. Both of these isotherms were treated theoretically in papers by Zel'dovich (17), Roginskiy (18), and Temkir (19). Kobozev and Gol'dfel'd as well as Temkin showed that the logarithmic isotherm can also be derived by assuming that adsorbed molecules repel each other on a homogeneous surface (20). As shown by Vol'kenshteyn (21), the parabolic isotherm can be explained by repulsion only if a type of interaction between adsorbed molecules which never occurs in nature is assumed.

It is more reasonable to ascribe deviations from the laws of simple and uniform adsorption to differences in active centers with reference to adsorption heat. The deviations from Langmuir's relationship cannot be explained by the interaction of adsorbed molecules, because the distances between them are too great.

Nikitin and Vdovenko (22) studied the dependence of adsorption of radium on glass from the concentration of radium ions in solution. Thirty to 60 minutes were sufficient to establish an adsorption equilibrium on the surface of a rotating glass cube. The coverage of the surface was very low, but a parabolic relationship applied.

A lowered p_H had the effect of reducing the quantity of radium which was adsorbed. Starik and Gurevich (23) observed a somewhat different dependence of radium adsorption on acidity and established that contamination with foreign ions has a strong effect on adsorption.

That the deviations from Langmuir's isotherm are due to inhomogeneities of the surface and consequent variation of the latter's adsorptive properties rather than to interaction between adsorbed molecules has been confirmed on the whole by experimental data obtained outside the USSR. Thus, O. Erbacher (Z. Phys. Chem. 1933, A. 163, 215; 1937, 180, 141; 1938, 182, 243; Z. Elektrochem., 1944, 50, 949) in determining the adsorption isotherms of natural radioactive isotopes of lead (thorium B), bismuth (thorium C), and polonium on silver, nickel, and gold, established that the ions in question are adsorbed according to a parabolic relationship (with $1/n < 1$) in the concentration range 10^{-7} — 10^{-2} mols per liter in the case of lead and polonium isotopes. The distance between the adsorbed ions of lead varies from 500 Å for the lowest concentration to 5 Å for the highest.

3. Adsorption of Mixtures

Nikitin and Ioffe studied the adsorption and desorption of radon on various grades of activated carbon of the AG brand (24). The influence of previously adsorbed benzene, water, and sulfur dioxide on the desorption of radon was investigated. Results obtained indicate inhomogeneous surfaces and exclude the action of repulsion forces between molecules. The adsorption of radon and of the tracer Ar^{37} on silica gel in the presence of carbon dioxide was also investigated. The partial pressure of carbon dioxide has no effect on the adsorption of argon. This indicates either that argon and carbon dioxide are adsorbed at different active centers, or that the centers which have the highest adsorption heat for argon exhibit the lowest adsorption for carbon dioxide.

- 4 -

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D. Differential Isotope Adsorption Method for Investigating Inhomogeneities of an Active Surface

The adsorption relationships at low coverage of the surface furnish indirect proof of surface inhomogeneity. Application of the differential isotope adsorption method permits a direct answer to the question of whether or not, from the point of view of its adsorption characteristics, a surface is homogeneous. The method was first suggested by Roginskiy in 1946(25). The first results referring to investigation of the surface of activated carbon were published by him in 1947(26). In 1948 the investigation was extended to typical catalysts, activated nickel and zinc oxide(27).

Molecules adsorbed on a homogeneous surface always are attached to the surface by an identical force. When there is increased density of adsorption, repulsive forces begin to act between molecules to an increasing extent. The force holding a molecule to the surface weakens, but always remains equal to that attaching another molecule to the same surface at the same time. This state of affairs is illustrated in Figure 1. If two portions of gas having a different isotopic composition are adsorbed on a surface of this type, the desorption will correspond to a uniform distribution of the isotopes on the surface, i.e., no change in the isotopic composition of the desorbed gas will occur. On an inhomogeneous surface (Figure 2) every active center has a different heat of adsorption and a different energy of adsorption activation; thus, the energy of desorption activation will vary correspondingly. If two portions of gas having a different isotopic composition are adsorbed on this surface, molecules which have the lowest activation energy of desorption will be desorbed first. Whether the molecules which were adsorbed first or those which were adsorbed later are the first to be desorbed depends on the relationship between the activation energy of adsorption and that of desorption for the molecules in question. This relationship may be symbatic, antibatic, or more complex. Experimental data pertaining to this question exist only on the activated adsorption of hydrogen by sugar carbon(28). Keyer and Roginskiy showed that this relationship appears to be complex under the specific conditions obtaining in this case: it is symbatic at a low density of adsorption and becomes antibatic at higher densities. The simplest case of a symbatic relationship between the activation energy of desorption E_{des} and the heat of adsorption Q_{ads} occurs in molecular adsorption when the activation energy of adsorption may be neglected and $E_{des} \sim Q_{ads}$. In this case the molecules which were adsorbed last will be desorbed first. If the relationship between E_{ads} and E_{des} is symbatic (Figure 3), the molecules adsorbed first will be desorbed first. Unless there is creeping on the surface, no redistribution with regard to the isotopic composition will occur, and that composition will vary as the gas is desorbed.

When light and heavy hydrogen (the stable isotope of hydrogen) were adsorbed on activated carbon made from sugar, gas having the isotopic composition of the second adsorbed portion was always desorbed first, independently of the order in which the two isotopes were adsorbed. Filling of the surface was 0.5 percent. The results show that at this density of adsorption creeping is absent. The equilibrium isotherm for hydrogen adsorption at minus 182 degrees corresponds to the parabolic equation $q = Ap^{0.75}$, indicating a pronounced degree of inhomogeneity with an exponential type of distribution of adsorption heats. In the case of nickel catalyst, light hydrogen and 99-percent deuterium were used. Independently of the order of adsorption, pure gas having an isotopic composition corresponding to that which was adsorbed last is desorbed first. After this follow fractions having a mixed composition; the pure isotope which was adsorbed first is desorbed last. These results again indicate a surface which is inhomogeneous with regard to adsorption. Zinc oxide both as adsorber and catalyst exhibits behavior which is incompatible with the assumption of a homogeneous surface (29; cf. also H. S. Taylor and S. Liang, J. Am. Chem. Soc. 69, p. 1306, 1947). Differential isotope adsorption shows definitely and directly that zinc oxide has an inhomogeneous surface and that, furthermore, the behavior in question cannot be due to mutual repulsion of molecules on a surface which is homogeneous

- 5 -

SECRET

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SECRET

50X1-HUM

with respect to adsorption. In the case of zinc oxide, gas having the isotopic composition of the second adsorbed portion is desorbed first, whereupon there is a sharp change to the composition of the other portion.

Similar results obtained with substances which differ from each other to the extent to which activated carbon, nickel, and zinc oxide do permit the generalization that deviations from Langmuir's type of adsorption must be due primarily to inhomogeneity of the surface with respect to adsorption.

II. APPLICATION OF TRACERS IN THE INVESTIGATION OF CATALYSIS

A. Effect of Promoters

Roginskiy and his collaborators showed that metals deposited by the vacuum vaporization method are inactive catalytically when foreign substances are completely absent at the time of deposition of the layer(30). Metal layers obtained in a gas stream (oxygen, nitrogen, or hydrogen) are activated by the content of gas acquired under those conditions. There is a maximum of catalytic activity corresponding to a gas content which is rather low (below 0.5 percent with reference to the weight of the metal). Using P_{32}^{32} with a half-life of 14.3 days (obtained by the nuclear reaction $S_{16}^{32} + n_0^1 = P_{15}^{32} + p_1^1$), Berezhneva, Oziraner, and Roginskiy prepared palladium catalysts containing phosphate ions which had been captured during the precipitation of the palladium. The effect of the promoter introduced in this manner is apparent from Figure 4. In the decomposition of hydrogen peroxide, the maximum promoter action occurs at a phosphorus content corresponding to 0.001 percent of the palladium weight. In the hydrogenation of ethylene, the maximum promoter action corresponds to 0.7 percent of phosphorus content. At the point of maximum promoter effect, the activity of the catalyst is ten times higher than that obtained without the promoter. By using the radioactive indicator method, the optimum concentration of the promoter can be determined very precisely, so that the exact quantity needed for the most effective action can be added to catalysts.

B. Investigation of the Mechanism of Catalytic Reactions

Two broad lines of investigation are being pursued here: one tests the hypothesis of the function of catalysts as transfer agents or, more generally, the hypothesis postulating the formation of an intermediate complex consisting of the catalyst and one of the active reaction components; the other is concerned with the succession of reaction stages on the catalyst surface, and the way these stages tie into each other.

An example of work along the first line is the study by Berezhneva and Roginskiy (5) of the interchange of bromine between ethyl bromide and ethylene bromide in the presence of $AlBr_3$ as a catalyst. Br_{82}^{82} with a half-life of 34 hours was used as tracer. Since both ethyl bromide and ethylene bromide interchange bromine atoms with aluminum bromide and since no exchange of bromine between the two organic compounds takes place in the absence of aluminum bromide, one must conclude that aluminum bromide actually functions as a transfer agent.

On the other hand, in the bromination of benzene with Br_2 in the presence of $ZnBr_2$ it could be shown that bromine atoms of zinc bromide are not transferred to benzene(31). Comparison of the kinetics of interchange of bromine atoms between $ZnBr_2$ and Br_2 with the kinetics of bromination of benzene shows that there is no connection between the two processes. The authors concluded that $ZnBr_2$ does not function as a transfer agent and that a deformation mechanism appears probable in this case.

- 6 -

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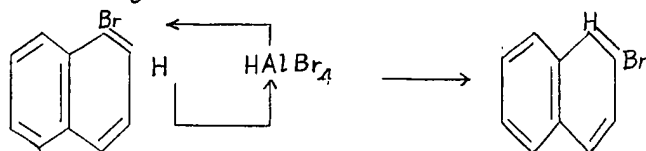
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Berezhneva and Roginskiy next studied the isomerization of alpha-bromonaphthalene to beta-bromonaphthalene in the presence of aluminum bromide(5). The isomerization does not take place in the absence of aluminum bromide. However, by using aluminum bromide tagged with a radioactive tracer it could be shown that the interchange between aluminum bromide and both bromonaphthalene isomers proceeds at a rate which is incompatible with the speed of the isomerization reaction. Consequently, there is no catalytic transfer of bromine in this case. Lyubarskiy (2) assumed that there is transfer of hydrogen over the catalytically active complex $AlBr_3$ according to the following scheme:



This is in keeping with results obtained by Moldavskiy and collaborators, who showed that the isomerization does not proceed with $AlCl_3$ or $AlBr_3$ alone in the absence of HCl or HBr (32).

In connection with research on reaction stages and the mechanism of catalytic reactions on surfaces, the theoretical treatment of the question by Roginskiy (33) must be mentioned. Roginskiy showed that these reactions are of the first order both for homogeneous and heterogeneous conversions. In the case of heterogeneous exchange reactions, this is true for both simple and complex surfaces. It follows from the essential simplicity of the reaction kinetics in this group of reactions that the dependence between the reaction mechanism and its operation in time is lost. Profound differences in the reaction mechanism are smoothed out and find no reflection in the time relationship. To clarify the true mechanism of catalytic interchange reactions, one must investigate the dependence of the reaction rate constant on the initial concentrations and the temperature within a wide range of changes of these variables. The theoretical conclusions outlined above do not apply when the reaction is of the diffusion type or when the surface is altered through catalyst poisoning or recrystallization. The use of tracer atoms in this line of investigation does not lead to unilateral results: several explanations are possible in many instances.

Successful application of differential isotope adsorption in the detection of the inhomogeneous nature of the surface of typical adsorption agents and catalysts has shown that this is a fruitful method of investigation (26, 27), especially since definite conclusions regarding the mobility of molecules and atoms on the surface can be drawn. Application of this method in catalytic reactions permits a study of the effect of surface inhomogeneity in these reactions. If two portions of the same gas having different isotopic compositions are adsorbed first, and the second reacting component is introduced afterwards, information in regard to the effect on the catalytic reaction of variations in the adsorptive activity of surface centers, i. e., of inhomogeneity with regard to heats of adsorption, will be obtained.

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- 7 -

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[Forty-four foreign references were also listed.]

[Figures follow.]

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- 8 -

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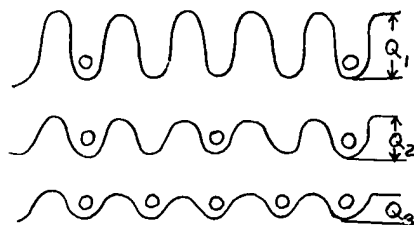


Figure 1. Representation of Homogeneous Surface under Assumption of Repulsive Forces Acting between Molecules

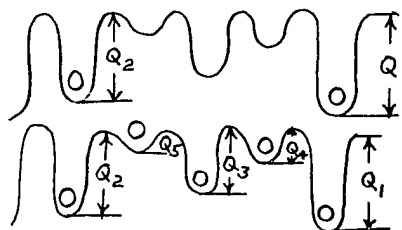


Figure 2. Representation of Inhomogeneous Surface

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- 9 -

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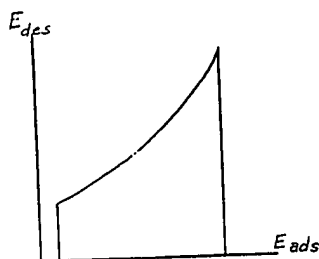


Figure 3. Example of Symbiotic Relationship between Energy of Adsorption and Energy of Desorption

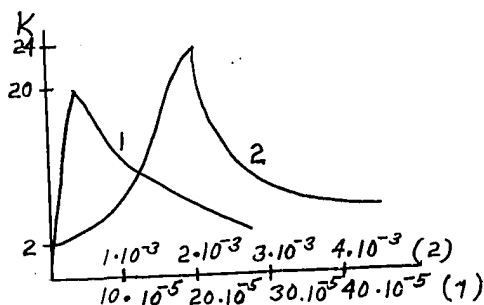


Figure 4. Effect of Phosphate Ions Captured during Precipitation of Metallic Palladium on Catalytic Activity of the latter

Curve 1 represents the catalytic decomposition of hydrogen peroxide. Curve 2 represents the catalytic hydrogenation of ethylene. The concentration of phosphorus with reference to the weight of palladium is plotted along the axis of the abscissae.

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- 10 -

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